Mordenite from Spain and its application as pozzolana

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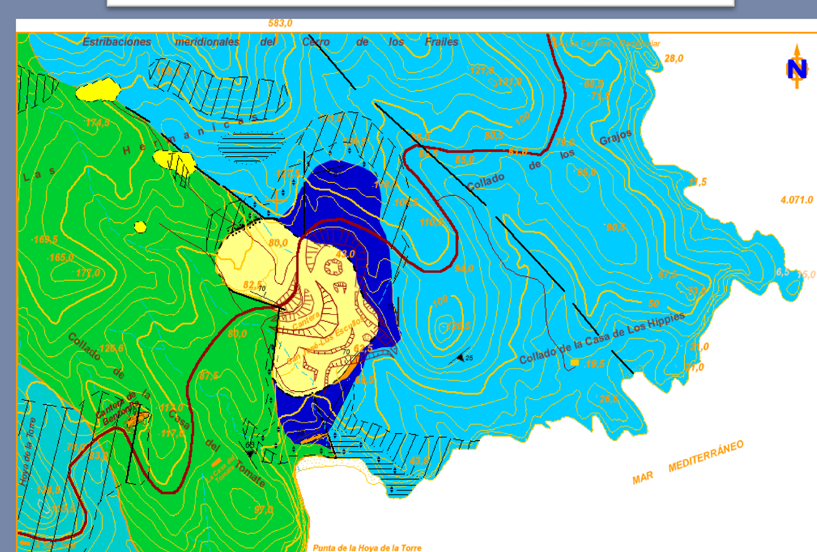
1. INTRODUCTION

In Spain, natural zeolites have been only found in the volcanic areas of Canary Islands (San Gil, M.M., 1959). However, several years ago the study of the South Eastern region of continental Spain (Cabo de Gata) revealed the presence of a deposit of mordenite being industrially commercialized as bentonite. The deposit San José-Los Escullos is located in the concession registered as Los Murcianos, managed by Bentonitas Especiales, S.A. (BENESA) who was extracting bentonite while ignoring the presence of the zeolite. The name San José-Los Escullos refers to the discovery of mordenite in this deposit. The deposit is located in a volcanic area, constituted by pyroxenic andesites, breccias, tuffs, pyroclasts with andesitic and dacitic composition, largely altered by the hydrothermal solutions. The recent discovery of this zeolite with mordenite content up to 97%, has changed the initial vision about that deposit, and new possible uses of this mineral in the pozzolanic cement industry are foreseen. This work intends to give preliminary data on the characterization of this zeolite according to X-ray diffraction (XRD), ICP analyses, and scanning electron microscopy (SEM), as well as to emphasize the pozzolanic properties of this material, using both chemical and mechanical tests.

2. LOCATION AND GEOLOGICAL SETTING

The only zeolite deposit studied in continental Spain, named San José-Los Escullos, is located in Almeria Province close to Rodalquilar, Los Escullos and San José district, over the coast line. Geographical coordinates are between 2º 4´ 08” W and 36º 46´ 42” N. The zeolite deposit is part of the main caldera complex of the southeastern volcanic region of Spain: Los Frailes, Rodalquilar, El Cinto y Lomilla de Las Palas, which are composed by a dacitic basement intruded and covered by dacitic domes, pyroxenic and hornblendic andesites, rhyolite and volcano-sedimentary materials (lapilli, tuff, ignimbrite, ash flow), in a wide hydrothermal alteration area. The composition of the volcanic area is mainly calc-alkaline. The main host rocks of the zeolitic mineralization are dacite and andesite. There is a strong metasomatic alteration in its contact with zeolite bodies, in which banded zeolite appears as a pseudomorphic product of both, plagioclase and pyroxene.



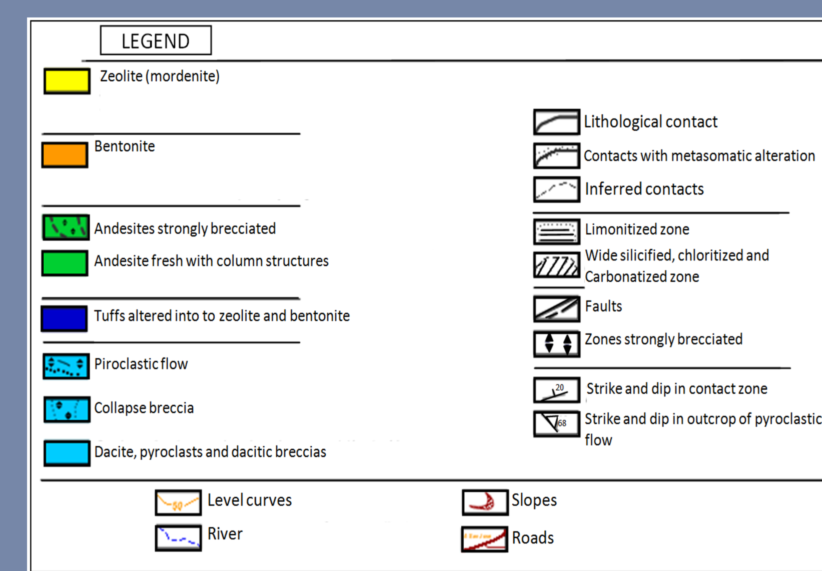


Figure 1. Geological map of the San José-Los Escullos deposit. Scale: 1:10.000 (Costafreda, J.L., 2008).

3. CHARACTERIZATION

Table 1 shows the chemical composition obtained from ICP (in weight %) showing a Si/Al ratio of 4.3 which lies in the range of 4 to 6, commonly observed in this type of natural zeolite, and a high content of Na^+; the corresponding approximate unit cell formula, excluding Fe, Ti and Mg contents and assuming that all the mineral corresponds to mordenite, is $Ca_{1.0}Na_{4.9}K_{1.8}Al_{8.6}Si_{39.4}O_{96}$.

Table 1:

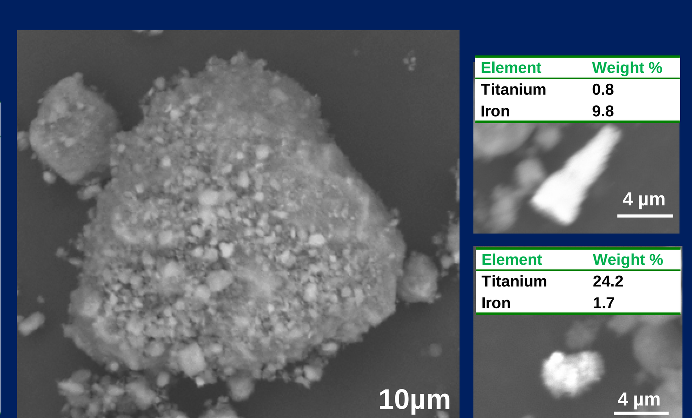
Al	Ca	Mg	Fe	K	Na	Ti	Si
6.2	1.0	0.4	0.9	1.9	3.0	0.1	28.5

From this data the final composition in oxides would be: SiO_2 61wt%; Al_2O_3 11.7wt%; Na_2O 4wt%; K_2O 2.3wt%; CaO 1.4wt%; MgO 0.7wt%; Fe_2O_3 1.3wt%; TiO_2 0.2wt%.

Scanning electron microscopy coupled with Energy Dispersive X Ray spectroscopy (Figure 2: SEM/EDX) revealed a homogeneous particle size distribution and consistent elemental composition. The higher Si/Al ratio obtained systematically by EDX could be due to the error associated to the technique which is only semi-quantitative.

Figure 2: SEM/EDX

Element	Weight %
Sodium	1.3
Magnesium	0.8
Aluminum	10.2
Silicon	76.5
Potassium	4.6
Calcium	2.2
Titanium	0.6
Iron	3.8



Impurities of Ti and Fe oxides as external particles could be identified.

Figure 3 shows the XRD profile which reveals a large amount of highly pure mordenite, with some impurities of smectite (S) and quartz (Q). Figure 4 plots the TGA and Derivative curves, where 10 % of water loss with a maximum desorption rate at temperatures around 100 ºC is observed.

Figure 3: XRD

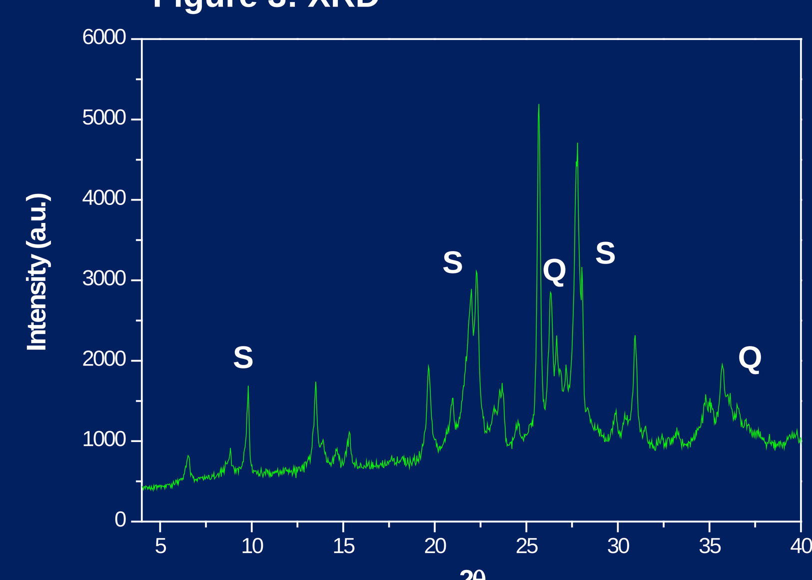
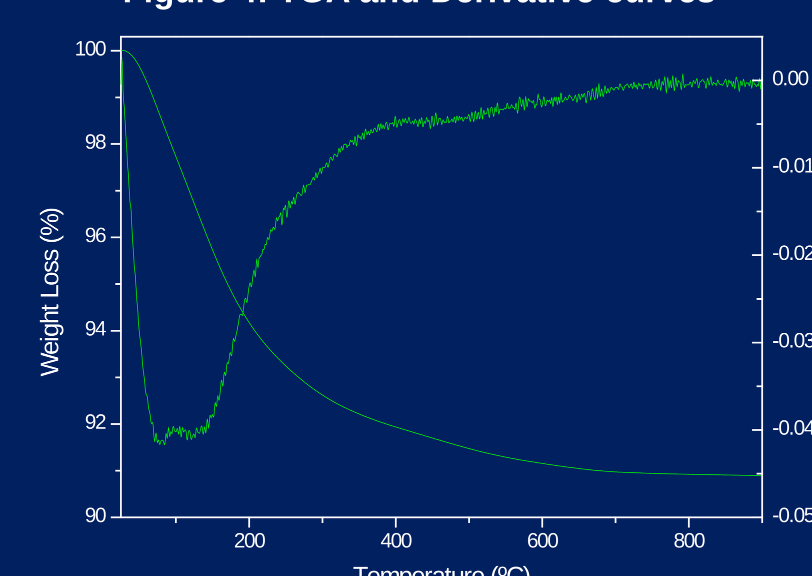


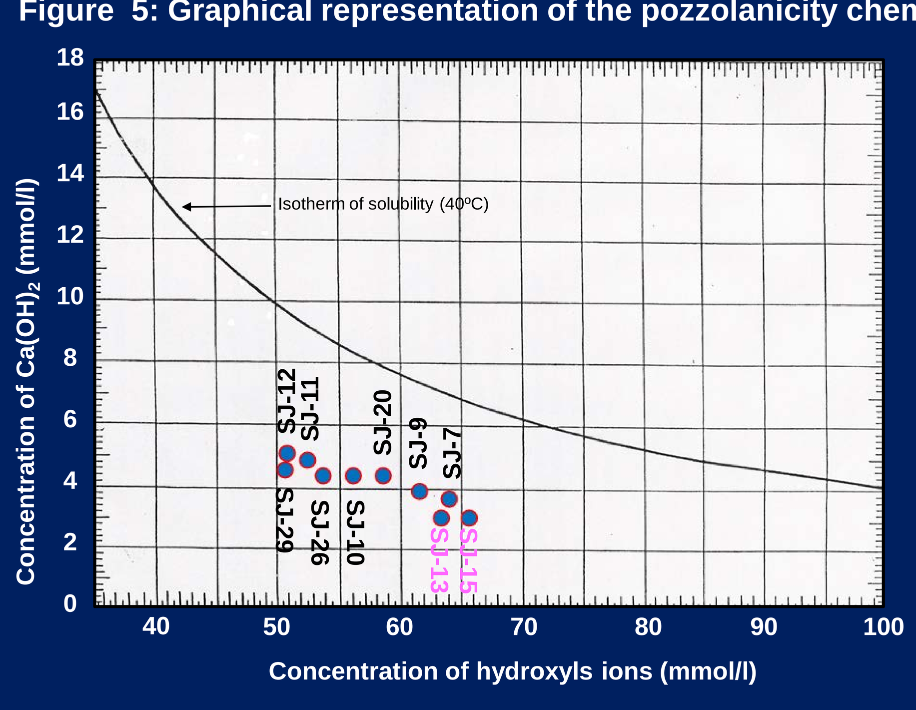
Figure 4: TGA and Derivative curves



4. APPLICATION AS POZZOLANA

Mordenite samples were analyzed randomly along the deposit of San José-Los Escullos (labeled SJ for San Jose, and 7-29 for sample number). The efficiency of the Spanish MOR as pozzolana was studied with electrical conductivity and chemical tests, allowing to establish an optimum to substitute partially the cement in ordinary mixtures in a ratio 75/25.

Figure 5: Graphical representation of the pozzolanicity chemical essay at 15 days.



The pozzolanic activity was determined according to EN 196-5:2006 by comparing the amount of $Ca(OH)_2$ required in an aqueous solution, to which a standardized portion zeolite pozzolanic cement was added, to obtain a saturated solution. The test is considered positive when the concentration of $Ca(OH)_2$ in the solution is lower than the saturation concentration at 40°C. The pozzolanic character of this Spanish zeolite was shown through a multistage process in the solid-liquid and solid-solid interface (zeolite + cement + water), which starts with the reaction between zeolite and portlandite ($Ca(OH)_2$) providing a new reaction product: the tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$). The appropriate reaction speed was reached due to previous sample crushing and grinding, up to grain sizes of 0.080 mm, 0.063 mm and 0.040 mm.

The cements made with zeolites were of the following classes:

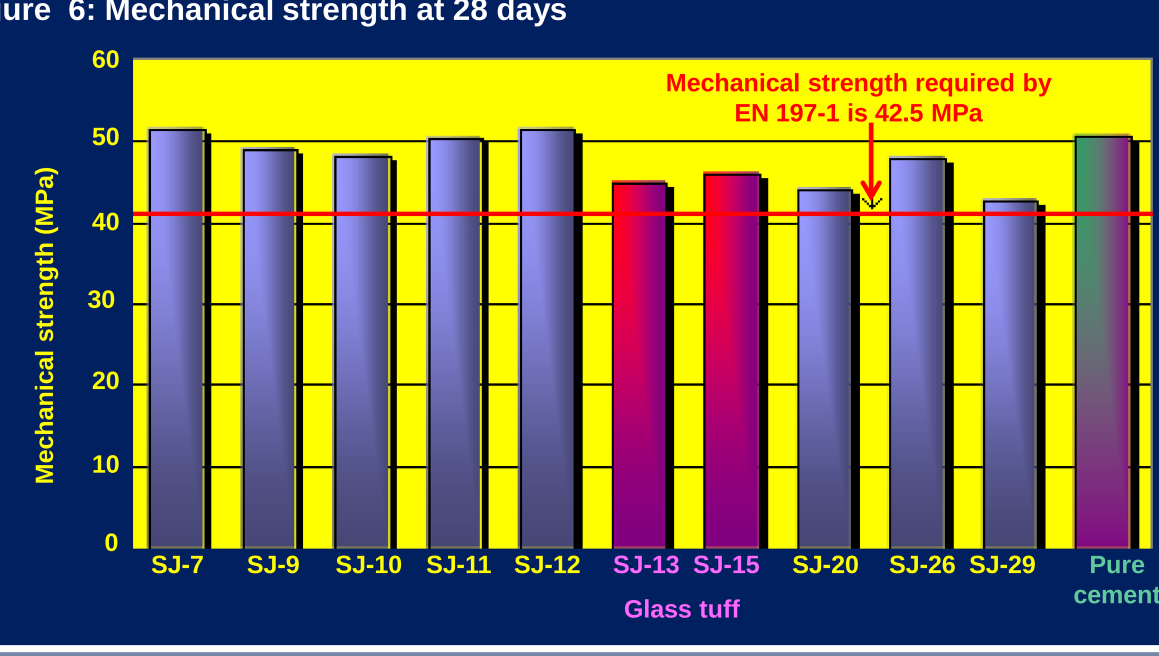
- Portland composite cement resistant to sulfates and to sea water (Type II/A-P and II/B-P- 42, 5 R/SR/MR).
- Pozzolanic cement with additives (Type IV/A and IV-B R/SR/MR)
- Composite cement (Type V/A R/SR)

The mortars obtained using zeolite mixtures showed great mechanical strength at 28 days (Figure 6), low density, high values of the Resistant Activity Index, and resistance against sulfates and sea water.

Table 2: Chemical composition by XRF of the mortars (zeolite + cement + sand + water) at 28 days. The XRF data of the parent zeolite used in SJ-7 (MOR) has been included for comparison purposes, also a pure cement built without zeolite (Cement)

	SiO_2	Al_2O_3	K_2O	Na_2O	MgO	Fe_2O_3	CaO	TiO_2	P_2O_5	SO_3	MnO
MOR	68.30	11.95	1.38	2.89	1.29	1.56	1.15	0.08	0.08	-	-
SJ-7	47.29	4.60	1.20	0.16	0.55	4.18	32.5	0.12	0.10	1.10	0.13
SJ-9	45.22	4.63	1.21	0.17	0.55	4.08	34.2	0.12	0.10	1.11	0.13
SJ-20	47.60	4.77	1.11	0.10	0.57	4.22	32.0	0.20	0.11	1.17	0.13
SJ-26	49.48	4.81	1.13	0.11	0.51	3.79	29.2	0.17	0.11	1.14	0.12
SJ-29	44.27	5.48	1.20	0.11	0.53	4.74	33.4	0.18	0.09	1.27	0.14
Cement	45.17	3.10	0.76	0.04	0.53	4.22	37.1	0.18	0.11	1.40	0.13

Figure 6: Mechanical strength at 28 days



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